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# Effect of $\text{TiF}_3$ catalyst on the tribological properties of carbon black-contaminated engine oils

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## ABSTRACT

The effects of a  $\text{TiF}_3$  catalyst on the tribological behaviour of carbon black-contaminated liquid paraffin and a fully formulated engine lubricating oil (CD SAE15W-40) were investigated using a four-ball tribological test. Scanning electronic microscopy with energy-dispersive spectroscopy, X-ray photoelectron spectroscopy, surface roughness, and thermogravimetric analyses were used to investigate the surface element content, chemical valence state, surface roughness, and initial decomposition temperature of the oil samples, respectively. Results showed that the average wear scar diameter (AWS) and friction coefficient of the two kinds of carbon black-contaminated lubricants decreased in the presence of 0.5 wt%  $\text{TiF}_3$ . The variation rates of the carbon black-contaminated liquid paraffin and fully formulated engine lubricating oil were 29.45% and 11.54%, respectively, and their initial decomposition temperatures decreased. These phenomena were ascribed to the decomposition of  $\text{TiF}_3$  catalyst into  $\text{TiO}_2$  and fluoride that resulted in the formation of improved boundary lubrication films. Moreover, for the fully formulated engine oil, the lubrication additive zinc dialkyldithiophosphate was catalyzed by  $\text{TiF}_3$ , decomposing into polyphosphate, which aided the formation of mixture boundary lubrication films.

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## 1. Introduction

The drive to save energy and reduce mankind's dependence on fossil fuels has promoted the development of a wide variety of alternative bio-derived fuels such as bio-ethanol, bio-diesel, and biomass pyrolysis fuel [1–5]. Engines powered by these fuels can benefit from reduced emissions and improved fuel economy. However, the generated soot, a by-product of the combustion process, cannot be eliminated easily [6]. Most of the soot generated during the combustion process is exhausted, but some can also contaminate the lubricant within the sump as a result of blow-by gasses, this can be worsened when exhaust gas recirculation is used [7,8]. Soot contamination of the lubricating oil can lead to increased wear in critical components as well as the shortening of oil life and increased frequency of oil changes. Thus, the importance of reducing the tribological impact of soot contamination within the lubricating oil is highlighted.

Soot contamination is a serious issue that has been extensively investigated by both engine and lubrication manufacturers. To

date, studies on engine soot mainly focus on soot formation and the associated wear mechanisms. However, the collection of soot particles to evaluate their tribological properties is difficult and very time consuming. Producing reliable data also depends on reproducing soot with consistent properties for use in contamination tests. To address these concerns, several studies have used carbon black, which simulates engine-derived soot. Ratoi et al. [9] used carbon black as engine soot dispersed in an engine oil, assessed the rapid removal of zinc dialkyldithiophosphate (ZDDP) reaction films by abrasion. However, this removal was limited (or even eliminated) by the choice of dispersant additive. Joly-Pottuz et al. [10] found that carbon black particles were highly abrasive between steel surfaces with increased wear and friction. However, they also found that the addition of carbon onions in a lubricant reduced both friction and wear. Olomolehin et al. [11] found that the combination of an alkyl ZDDP and carbon black produced aggressive wear in test samples. They also showed that a lubricant containing carbon black and a ZDDP additive lead to considerably more wear than without the ZDDP additive. Green and Lewis used carbon black simulated engine soot to investigate the oil properties and wear of engine components. They attributed soot wear mechanisms to an engine soot abrasion effect [12–14]. These studies indicate that carbon black can be used as a substitute for engine soot to investigate the friction and wear properties of

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lubricating oil. Many studies have been conducted to investigate the soot induced wear of engine parts with the different tribological tester [15–18]. They indicate that low levels of carbon black can play an important role in strengthening the antiwear properties of an engine's lubricating oil [13]. The wear effects of carbon black-contaminated lubricating oils on the critical components of engine frictional parts can be decreased by the optimization of a dispersant and solid lubricant. The carbon black used in the present tribological study is a good substitute for engine soot based its morphology, composition, and particle size [19].

Solid fluorine catalysts have been shown to reduce the wear effect of carbon black-contaminated lubricating oils. For example, Nehme [20,21] showed the significant effect of an  $\text{FeF}_3$  catalyst on the performance of plain ZDDP oil. The tribological and chemical interactions of ZDDP/ $\text{FeF}_3$  underlying their improved wear performances have also been examined with high performance lubricants and modified PTFE coating on metal surfaces by Elsenbaumer et al. [22]. Mourhatch and Aswath [23,24] used different contact loads and performed several chemistry characterization studies to differentiate the wear mechanisms of ZDDP plain oil and ZDDP oil in the presence of  $\text{FeF}_3$ . Huq and Aswath [25] used a TEM to investigate the anti-wear film/wear particles generated in the present of  $\text{TiF}_3$  catalyst under boundary lubrication condition. Parekh [26] examined the chemical interactions between ZDDP and  $\text{FeF}_3$  that yielded a new chemical species responsible for the improved wear performance. There have also been patents registered regarding the use of transition metal fluorides as additives to enhance the activity of ZDDP (see for example Shaub et al. and Aswath et al. [27,28]). Greer [29] suggested that oil ingredients can be catalyzed with appropriate fluorinated materials. As is well known, both  $\text{TiF}_3$  and  $\text{FeF}_3$  catalysts can reduce the gas emissions, and also can be used to promote the degradation of ZDDP. This would result in improved antiwear and antifricition properties for engine oils as well as a reduction in sulfur and phosphorous levels.

However, studies on the use of metal fluorides in simulated engine soot-contaminated lubricating oil are limited. As are studies on methods for decreasing the destructive effect of carbon black (soot) contaminated lubricating oil. Therefore, this paper describes a study of the effects of a  $\text{TiF}_3$  catalyst (0.5 wt%) on the tribological behavior of (1 wt%) carbon black-contaminated liquid paraffin and a fully formulated engine lubricating oil (CD SAE15W-40). A series of comparison experiments were designed to address the efficacy of  $\text{TiF}_3$  catalyst material to decrease engine soot wear. A systematic approach was used to establish basic wear data and subsequent methods for optimizing the formulation of engine oil with soot.

## 2. Experimental

### 2.1. Materials and sample preparation

Commercially available carbon black (CB; Cabot N660R, Shanghai Cabot Chemical Industry Co. Ltd., China) was used as an engine soot alternative. Fig. 1 shows the morphology, chemical composition, and particulate diameter of the CB. These characteristics were compared to true engine soot harvested from the combustion of 0# diesel (Hefei Petrochemical Company, China). They were taken using a HRTEM (high resolution transmission electron microscopy) and show the average particulate diameter sizes and degrees of crystalline for the CB and soot particulates. The average particle diameter of carbon black was 40 nm, and engine soot was 45 nm. The inset diffraction patterns of two carbonaceous materials indicated that a large amount of amorphous carbon existed. The two carbon materials had virtually indistinguishable perturbed graphitic or turbostratic internal structures.

A commercially available  $\text{TiF}_3$  catalyst was purchased from Alfa-Asia Tianjin Chemical Co., Ltd. Fig. 2 shows the morphology and chemical composition of  $\text{TiF}_3$ .

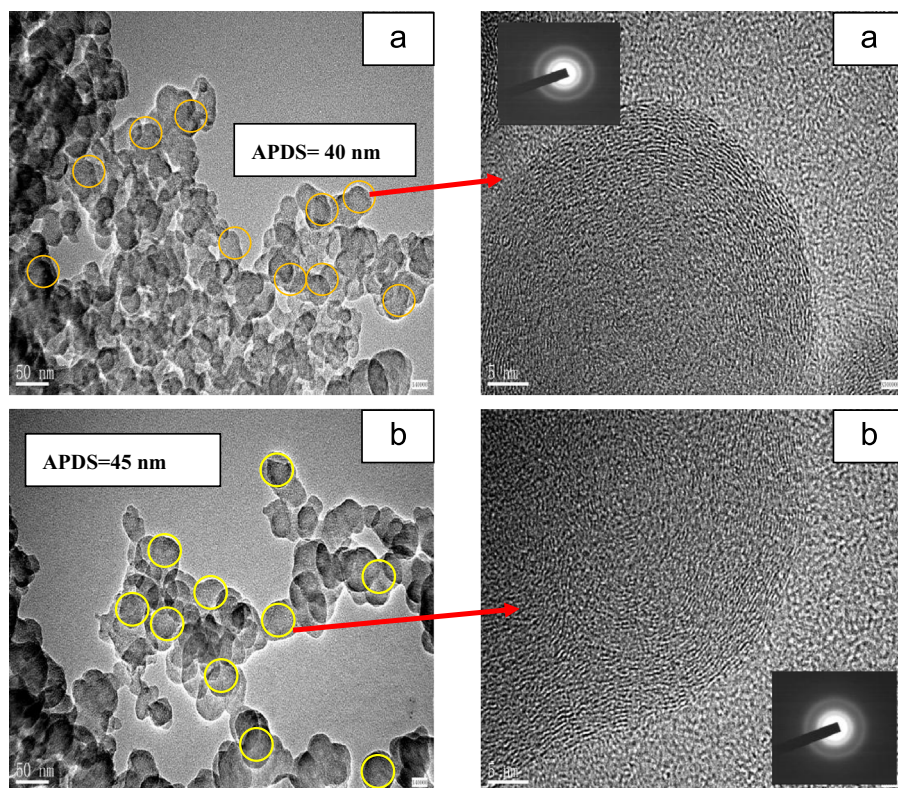


Fig. 1. HRTEM images of carbon black and engine soot: (a) carbon black, (b) engine soot.



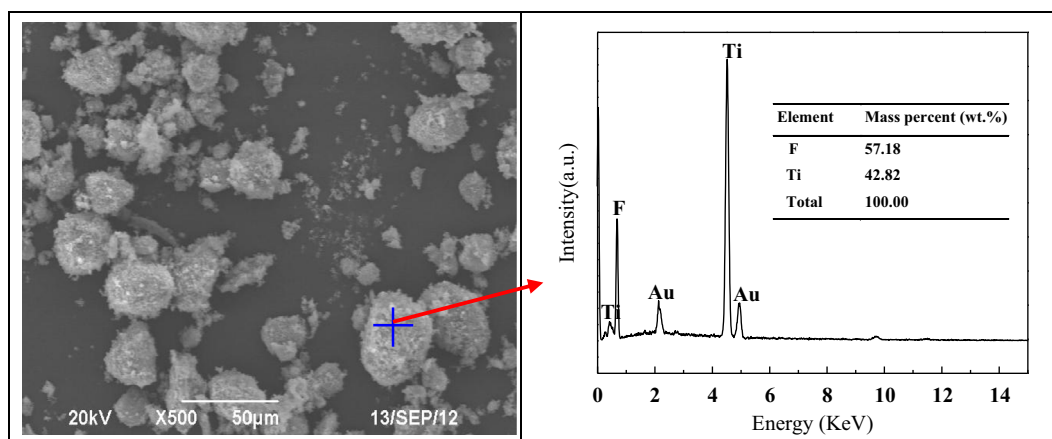


Fig. 2. SEM and EDS analysis of  $\text{TiF}_3$ .

**Table 1**  
Physicochemical properties of base oil and engine oil.

Item	Liquid paraffin	CD SAE 15W-40	Methods
Density ( $\text{kg/m}^3$ )	0.88	0.85	ASTM D4052
Kinematic viscosity ( $\text{mm}^2/\text{s}$ , 40 °C)	100	110.6	ASTM D445
Viscosity index	98	142	ASTM D2270
Sulfur content (wt%)	No	2.5%	ASTM D4294
Phosphorus content (wt%)	No	0.1%	ASTM D1091
Water (m/m) %	Trace	Trace	ASTM D6304
Pour point (°C)	−15	−24	ASTM D9
Flash point (°C)	210	220	ASTM D93
Acid number ( $\text{mg KOH g}^{-1}$ )	0.014	0.035	ASTM D664

A base oil liquid paraffin (LP; Hengshui Diyi Petrochemical Co., Ltd.) and a fully formulated engine lubricant (CD SAE 15W-40, Sinopec Lubricant Company) were used for this investigation. Their physicochemical properties were measured according to the American Society of Testing Materials (ASTM) standards, as shown in Table 1.

The other reagents such as acetone and ethanol were analytical grade. Tribological tests were conducted using a four-ball tribometer (MQ-800) [30]. The steel balls used in the tests were ASTM E2100 grade bearing steel with a diameter of 12.7 mm, fabricated according to the GB/T 308–2002 national standard of China, and heat treated according to the national mechanical standard of China (JB/T 1255–2001). The hardness was  $\text{HRC}=65$  and surface roughness  $R_a=0.012 \mu\text{m}$ . The liquid paraffin oil samples were prepared with 0 wt% CB+0 wt%  $\text{TiF}_3$ , 1 wt% CB, 0.5 wt%  $\text{TiF}_3$ , and 1 wt% CB+0.5 wt%  $\text{TiF}_3$ . The CB and catalyst were dispensed with vigorous stirring for 2 h throughout the oil, followed by ultrasonication for 30 min to reduce experimental deviation. The CD SAE 15W-40 samples were prepared in a similar manner.

## 2.2. Characterization

Tribological tests were at room temperature (approximately 25 °C) according to ASTM D5183–2005 and the procedure described in [31]. The wear and friction properties of the contaminated oils were investigated at 1450 rpm and 196 N load (maximum Hertzian contact pressure = 2.74 GPa) for 30 min. Prior to the tribological tests, all oil samples were again placed in an ultrasonic bath for 30 min to reduce experimental deviation. Optical microscopy was used to obtain the average wear scar diameter, and a scanning electron microscopy–energy-dispersive spectroscopy (SEM/EDS) system (JEOL Model JSM-6490) was used

to observe the surface morphology and elemental composition of the wear scar area. A surface roughness measurement system (Taylor-Hobson-6) was used to measure the surface roughness of the wear scar on the top surface of the steel ball under  $10,000\times$  magnification. The length of the sample was 0.08 mm, and the evaluation length was five times the sample length using a Gaussian filter and a steel ball sensor of 10,000:10 mm.

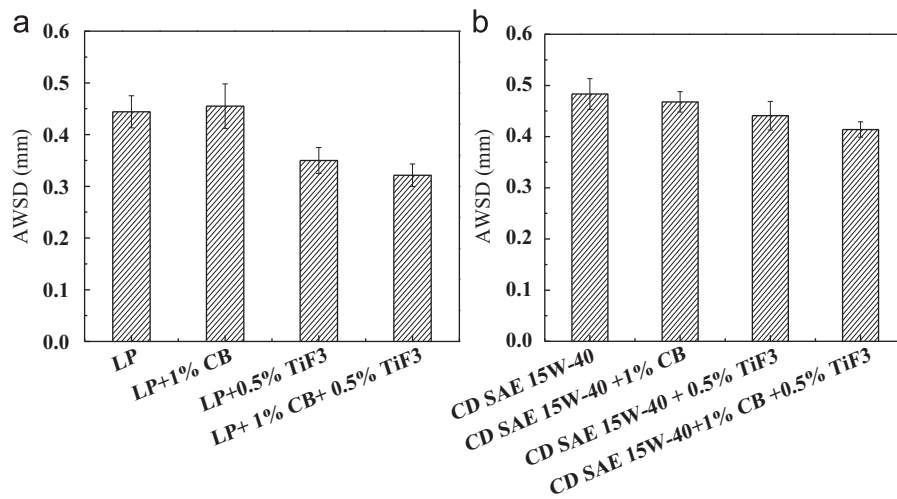
To distinguish the influential mechanism of the  $\text{TiF}_3$  catalyst on the tribological behaviors of engine carbon black-contaminated engine lubricants, an X-ray photoelectron spectroscopy system (ESCALAB250) and a thermogravimetric analyzer (Q5000IR) were used to investigate the elemental chemical valence state in the wear zones of steel balls and the variations in thermal properties of the oil samples, respectively. Oil samples (5 mg to 10 mg) were placed in a platinum pan and heated from 35 °C to 800 °C at a heating rate of 10 °C/min under 8 mL/min oxygen purge.

## 3. Results and discussion

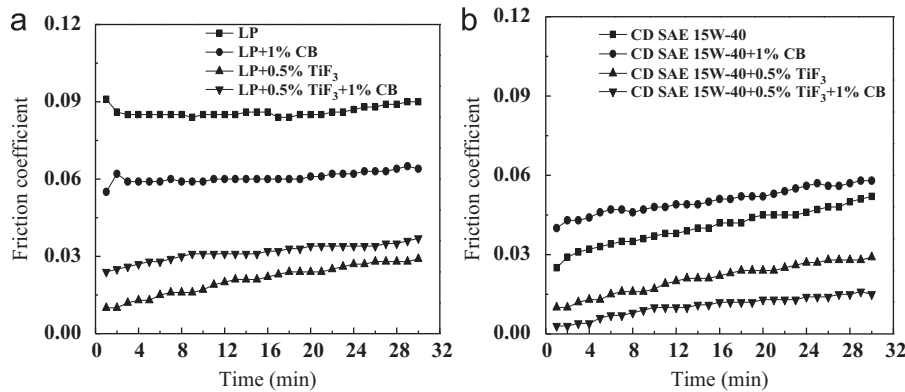
### 3.1. Wear resistance

Fig. 3 shows the wear resistances of the oil samples. Fig. 3(a) shows the variations in average wear scar diameter of liquid paraffin with and without  $\text{TiF}_3$  catalyst. The AWSD of pure liquid paraffin was 0.444 mm. For the liquid paraffin with 1.0 wt% CB the AWSD was 0.455 mm. This indicates that the CB has little effect on the antiwear properties of liquid paraffin. However, the AWSD decreased to 0.321 mm when the  $\text{TiF}_3$  catalyst was added, indicating that  $\text{TiF}_3$  particles can improve the antiwear properties of carbon black-contaminated liquid paraffin. The addition of the  $\text{TiF}_3$  catalyst in uncontaminated liquid paraffin was also investigated. The results show an AWSD of the pure liquid paraffin increased when compared to the contaminated oil. The lowest observed AWSD was that of the liquid paraffin with 1 wt% CB and 0.5 wt%  $\text{TiF}_3$ . This phenomenon indicated that CB particles make a contribution to the antiwear property of liquid paraffin. In all,  $\text{TiF}_3$  catalyst material had an important function in strengthening the antiwear properties of liquid paraffin and carbon black-contaminated liquid paraffin.

Fig. 3(b) shows the variations in AWSDs of CD SAE 15W-40 with and without the addition of the  $\text{TiF}_3$  catalyst. The AWSD of the uncontaminated lubricant was 0.483 mm, but for the CB-contaminated CD SAE 15W-40 this decreased to 0.4678 mm. The addition of 0.5 wt%  $\text{TiF}_3$  further reduced the AWSD to 0.4138 mm, which was lower than that of carbon black-contaminated CD SAE 15W-40 lubricant. These results again indicate that the  $\text{TiF}_3$



**Fig. 3.** Variations in the average wear scar diameter of carbon black-contaminated liquid paraffin and CD SAE 15W-40 oil with and without TiF<sub>3</sub> catalyst (0.5 wt%) at 196 N load and 1450 rpm rotation speed for 30 min (a) LP (b) CD SAE 15W-40.



**Fig. 4.** Variations in friction coefficient of carbon black-contaminated liquid paraffin and CD SAE 15W-40 oil with and without TiF<sub>3</sub> catalyst (0.5 wt%) at 196 N load and 1450 rpm rotation speed for 30 min (a) LP (b) CD SAE 15W-40.

catalyst plays an important role in reducing wear. The findings for the CD SAE 15W40 lubricant were similar to those for liquid paraffin, i.e., 0.5 wt% TiF<sub>3</sub> catalyst addition reduced the wear of engine oil and carbon black-contaminated engine-lubricating oils.

### 3.2. Friction reduction

Fig. 4(a) shows the variations in the friction coefficient of liquid paraffin with and without the TiF<sub>3</sub> catalyst. The friction coefficient of pure liquid paraffin was higher than both of liquid paraffin added with 1.0 wt% CB and 0.5 wt% TiF<sub>3</sub> catalyst. This is likely to be the result of the poor friction reducing properties of the liquid paraffin component. The addition of 1 wt% CB to the liquid paraffin caused the friction coefficient of oil to decrease and this is likely to an effect of the “roll effect” of dispersed CB particles, similar to that of Green [13]. Adding 0.5 wt% to CB contaminated liquid paraffin caused the friction coefficient to decrease further. This indicates that the TiF<sub>3</sub> catalyst caused a significant reduction in friction. A similar reduction in frictional was also observed when the TiF<sub>3</sub> catalyst was added to pure liquid paraffin.

Fig. 4(b) shows the variations in friction coefficient of CD SAE 15W-40 lubricant samples. The friction coefficient of carbon black-contaminated CD SAE 15W-40 lubricant was higher than that of pure lubricant. The possible reason for this was that the soot absorbed additives and exerted agglomeration effects within the lubricant [32]. When 0.5 wt% TiF<sub>3</sub> catalyst was added to the CB contaminated lubricant, the friction coefficient decreased. This

result once again indicates that the TiF<sub>3</sub> catalyst significantly reduced friction. To further verify the cause of these observations the TiF<sub>3</sub> catalyst was once again added to pure CD SAE 15W40, and the result indicated that this catalyst material did reduce friction.

The above observations indicate that TiF<sub>3</sub> catalyst plays an important role in reducing friction for the liquid paraffin and fully formulated lubricating oil, both with and without CB contamination.

### 3.3. Surface analysis

The surface morphologies of the wear zones of steel test samples were observed with an SEM/EDS system to determine whether the simulated soot particulates would promote the wear. Table 2(a) shows the images taken from the surfaces steel balls lubricated using pure liquid paraffin. The black arrows and rectangle represent the striking furrows and grooves on the surface of the wear zone. These are the result of the higher kinematical viscosity of liquid paraffin, causing adhesive wear to occur during the rubbing process. The surface roughness was 0.040 μm, which indicated that the wear of pure liquid paraffin was severe. Table 2(b) shows images of surface morphologies of steel balls using the CB contaminated liquid paraffin. Numerous furrows with broken edges (black arrows) were observed. This phenomenon could be attributed to the fact that carbon black particles were scratching the surfaces. When 0.5% catalyst TiF<sub>3</sub> was added to the CB contaminated liquid paraffin, surface

**Table 2**  
Surface roughness and images of steel balls after rubbing for 30 min under different conditions.

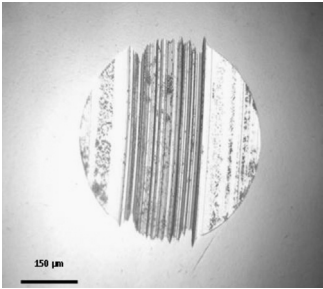
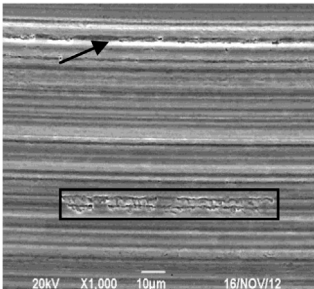
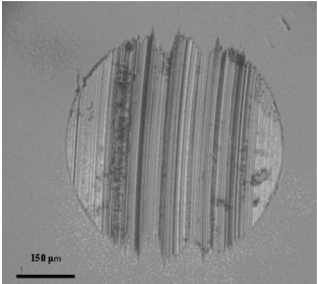
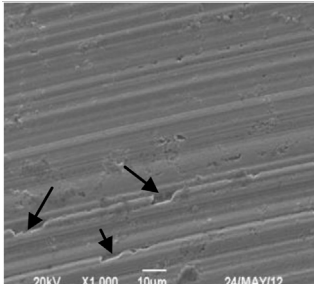
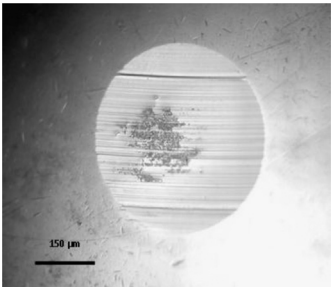
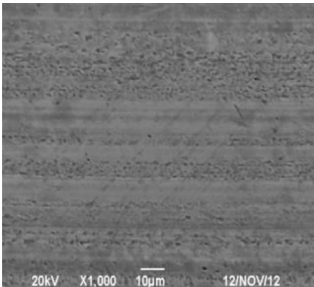
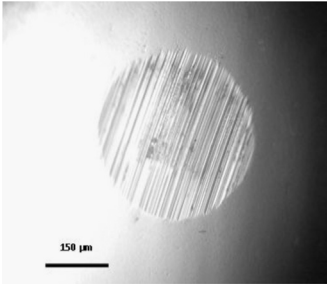
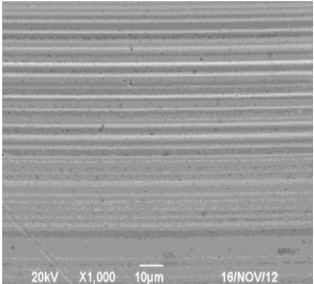
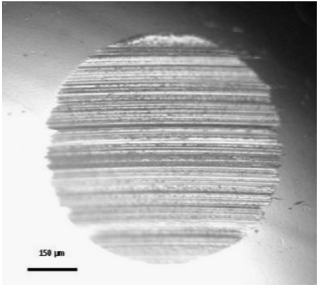
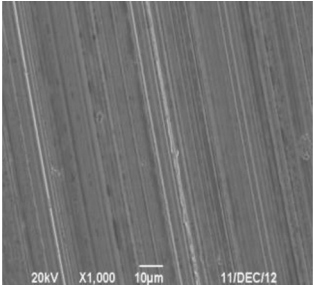
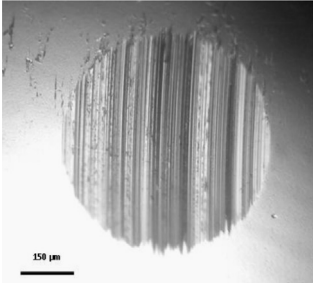
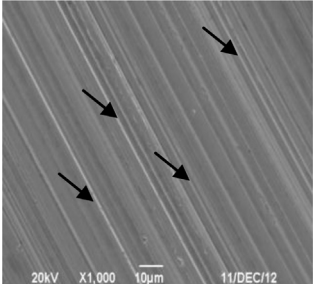
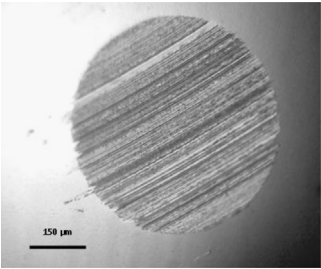
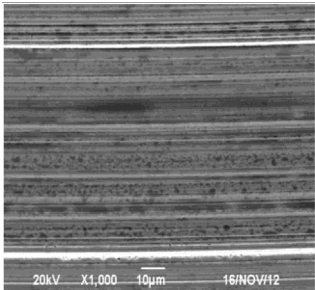
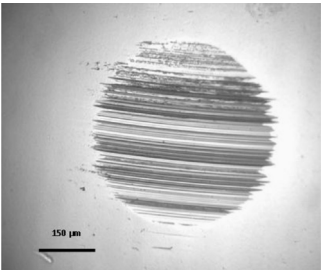
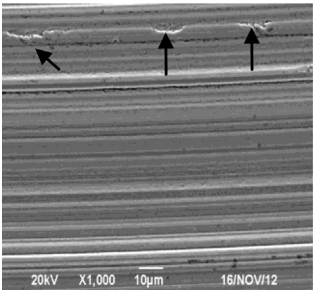
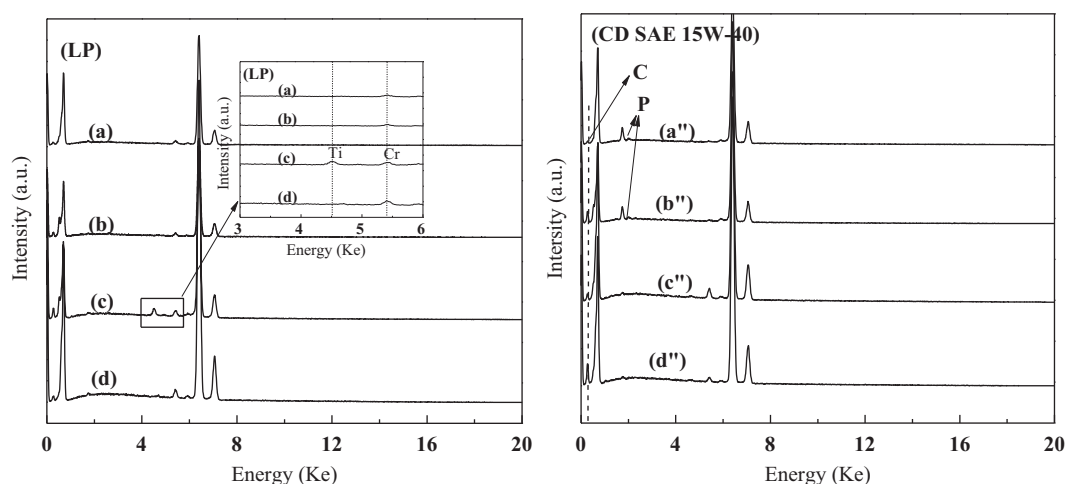
Code	Stationary ball	Rotational ball	Surface roughness (μm)
a			0.040
b			0.050
c			0.015
d			0.020
e			0.055
f			0.033

Table 2 (continued)

Code	Stationary ball	Rotational ball	Surface roughness ( $\mu\text{m}$ )
g			0.026
h			0.037

Notes: (a) LP, (b) LP+1 wt% CB, (c) LP+0.5 wt%  $\text{TiF}_3$ , (d) LP+1 wt% CB+0.5 wt%  $\text{TiF}_3$ , (e) CD SAE 15W-40, (f) CD SAE 15W-40+1 wt% CB, (g) CD SAE 15W-40+0.5 wt%  $\text{TiF}_3$ , and (h) CD SAE 15W-40+1 wt% CB+0.5 wt%  $\text{TiF}_3$ .



**Fig. 5.** EDS analysis of the wear zones of the two oil samples after rubbing for 30 min (1450 rpm rotation speed and 196 N load). (a) LP (b) LP+1% CB (c) LP+0.5%  $\text{TiF}_3$  (d) LP+1% CB+0.5%  $\text{TiF}_3$ . (a'') CD SAE 15W-40 (b'') CD SAE 15W-40+1% CB (c'') CD SAE 15W-40+0.5%  $\text{TiF}_3$  (d'') CD SAE 15W-40+1% CB+0.5%  $\text{TiF}_3$ .

morphologies of the wear zones revealed a reduction in surface roughness to  $0.020 \mu\text{m}$ . The furrows that appeared on the wear zone were less severe than those for the pure liquid paraffin and CB contaminated liquid paraffin in Table 2(d). To further examine the antiwear and antifriction properties of the  $\text{TiF}_3$  catalyst, it was added to pure liquid paraffin. Results indicate that the surface roughness decreases continually, and the furrows disappear in the wear zone in Table 2(c). Therefore 0.5 wt%  $\text{TiF}_3$  catalyst addition to liquid paraffin can reduce simulated-soot wear.

Table 2(e) reveals the surface morphological images of steel balls of pure CD SAE 15W-40 oil. The appearance of furrows was easily observed on the surface of the rotational ball. The surface roughness was  $0.055 \mu\text{m}$ . Table 2(e–h) shows images of wear scar morphologies of fully formulated engine oil. The surface furrows (Table 2(f)) suggest that wear is more severe than for pure CD SAE 15W-40 oil (Table 2(e)), but surface roughness's were lower. This phenomenon could be due to the fact that local carbon black

reunion or undispersed carbon black particles exacerbated wear, this would be consistent with the friction coefficient results. Surface roughness decreased compared to pure SAE CD 15W-40 oil when 0.5 wt%  $\text{TiF}_3$  catalyst was present. These results indicated that  $\text{TiF}_3$  catalyst strengthens the antiwear and antifriction properties of carbon black-contaminated CD SAE 15W-40 oil.

Fig. 5 shows the variations in element contents in the wear zone for the two kinds of oil tested. The inset in Fig. 5(a) signified that elemental titanium was absorbed onto the wear surfaces during the friction process. Titanium and fluorine elements were not observed when the  $\text{TiF}_3$  catalyst (0.5 wt%) was added to the carbon black-contaminated liquid paraffin. This observation was due to the low contents of these elements. Fig. 5(b) reveals that elemental phosphorus was observed on the wear pair without the  $\text{TiF}_3$  catalyst in the fully formulated engine lubricant. This result indicated that the additives played an important role in antiwear and friction reduction efficiency. Elemental phosphorus was not



**Table 3**

Element atomic contents of the wear zones of selected steel ball samples after rubbing for 30 min (rotation speed, 1450 rpm; load, 196 N).

Samples	Atom content (at%)							
	C	O	Fe	P	Ti	F	Zn	Ca
LP	42.94	45.82	11.28	0	0	0	0	0
LP+1% CB	63.55	30.77	5.68	0	0	0	0	0
LP+0.5% TiF <sub>3</sub> +1% CB	62.42	30.27	5.64	0	0.7	0.97	0	0
CD SAE 15W-40+1% CB	50.34	37.24	11.19	1.23	0	0	0	0
CD SAE 15W-40+0.5% TiF <sub>3</sub> +1% CB	50.32	35.67	6.02	2.97	0.9	1.81	0	2.31

**Table 4**

EDS analysis of extracted carbon black particles.

Items	Element content (wt%)								
	C	O	Fe	P	S	Ti	F	Cr	Ca
LP+1 wt% CB	71.08	17.93	10.99	–	–	–	–	–	–
LP+1 wt% CB+0.5 wt% TiF <sub>3</sub>	73.39	9.48	3.57	–	–	2.94	10.62	–	–
SAE CD 15W-40+1 wt% CB	75.67	11.49	6.35	1.71	4.45	–	–	0.33	–
SAE CD 15W-40+1 wt% CB+0.5 wt% TiF <sub>3</sub>	28.68	25.05	3.20	0.44	1.42	18.57	22.64	–	–

found when the TiF<sub>3</sub> catalyst was added to CD SAE 15W-40 lubricant, which was likely due to its low content. These results suggest that the TiF<sub>3</sub> catalyst material significantly contributed to the formation of a boundary lubrication film.

To further examine the effect of the TiF<sub>3</sub> catalyst on the tribological behaviors of the CB contaminated engine oils, X-ray photoelectron spectroscopy and thermogravimetric analysis were used to investigate the wear zones and oil samples. Table 3 shows the variations in elemental content in the wear zones with and without the TiF<sub>3</sub> catalyst. Titanium and fluorine elements were detected when 0.5 wt% TiF<sub>3</sub> was added to the CB contaminated liquid paraffin. Similarly, these two elements along with phosphorus were detected in CD SAE 15W-40 oil. Elemental sulfur was not detected in the SAE CD 15W-40 oil with 1 wt% CB. The reason for this was possible due to the low content of ZDDP, which would have caused the absorptive CB particles or by an “abrasion effect” from the agglomerated carbon black particles [33,34]. The Absorption effect could be expounded via the component analysis of the extracted carbon black particles, given in Table 4. Titanium, fluorine and phosphorus were detected when the 0.5 wt% TiF<sub>3</sub> was added. This indicated that the TiF<sub>3</sub> absorbed the ZDDP molecules to form a mixed/boundary lubrication film. The appearance of titanium and fluorine in the wear zones indicated that the TiF<sub>3</sub> catalyst made some contribution to the efficiency of the antiwear and antifricition of the lubricants. It also indicated that titanium and fluorine elements can also assist in the formation of a boundary film. The detailed element chemical valence states are shown in Fig. 6. The results of C1s spectral analysis (Fig. 6(a)) showed that the binding energy at 284.8 eV was attributed to C–C and C–H, and the peak at 286.3 eV was attributed to C–O–C and C–O–H. The peak at 288.9 eV was C=O and O–C–O [35]. Table 5 shows the variations in functional group contents (C–C, C–O, and C=O). The C–O and C=O contents obviously increased in the presence of the catalyst in liquid paraffin [36]. This result was possibly due to oxidation and degradation effects. In the CD SAE 15W-40, the C–O content decreased because of oxidization resulting from the increase in C=O (Fig. 6(b)). The O1s spectra (Fig. 6(c and d)) indicated the formation of a boundary film containing different types of oxidized metals or phosphates.

The binding energy at 707 eV and 720 eV was attributed to Fe 2p characteristic peaks, and the peak at 710.8 eV was attributed to Fe<sub>2</sub>O<sub>3</sub>. The Fe 2p spectra (Fig. 6(e)) showed that the iron atoms changed into iron oxides (such as Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>) in the pure

liquid paraffin and with 1 wt% CB. This result indicated that iron atoms were subject to oxidative reactions on the rubbing surfaces. Iron atoms (BE=707 eV) did not completely change into iron oxides in the presence of 0.5 wt% TiF<sub>3</sub> catalyst (Fig. 6(e)). This phenomenon indicated that the iron atoms were protected via the lubrication film.

Moreover, the Ti 2p spectra (Fig. 6(g)) showed that the binding energies at 457.88 eV and 463.5 eV were the characteristic peaks of TiO<sub>2</sub>. The F1s spectrum (Fig. 6(i)) showed that the only peak at 684.9 eV belonged to fluoride [37]. These results indicated that the boundary lubrication film contained titanium, fluorine, and carbon elements.

Phosphorus, titanium and fluorine elements were detected when the catalyst was added to CD SAE 15W-40 lubricant. Table 3 shows the elemental atom contents. The contents of phosphorus, fluorine, and titanium with catalyst addition were higher than those of samples without it. The Ti 2p spectra (Fig. 6(h)) showed two peaks at 457.88 eV and 463.5 eV, which were attributed to TiO<sub>2</sub>. The F1s spectra (Fig. 6(j)) indicated the existence of fluoride. The P 2p spectra (Fig. 6(k)) of the wear zone showed only one peak at 133.2 eV, which belonged to phosphate. These results suggest that the improvements of antiwear and antifricition of CB contaminated SAE CD 15W-40 oil with 1 wt% carbon black and 0.5 wt% TiF<sub>3</sub> were attributed to the synergistic effect of ZDDP and the TiF<sub>3</sub> catalyst material. The wear mechanism was attributed to the participations of titanium, fluorine and phosphate during the formation of boundary lubrication film.

### 3.4. Wear mechanism analysis

The antiwear and antifricition of carbon black-contaminated liquid paraffin and formulated engine lubricant were ascribed to the formation of boundary lubrication films containing carbon, titanium, and fluorine elements. Fig. 7 shows the schematic diagram of tribofilm formation for liquid paraffin and CD SAE 15W-40 lubricant in the presence of the TiF<sub>3</sub>. The active components of titanium and fluorine in the oils were physically absorption in significant amounts on the surfaces of steel balls [38]. During the rubbing process, the chemical reaction for wear played an important role in the formation of a boundary lubrication film. This can be used to explain the antiwear and antifricition mechanisms of CB contaminated engine oils in the presence of the TiF<sub>3</sub> catalyst. The chemical valence state of the titanium was changed



from  $\text{Ti}^{3+}$  to  $\text{Ti}^{4+}$ . This phenomenon indicated that the  $\text{TiF}_3$  catalyst decomposed into  $\text{TiO}_2$  and fluorates, which have better lubrication properties [39,40].

The fully formulated engine oil containing different kinds of lubrication additives such as ZDDP can form a better boundary

lubrication film than liquid paraffin oil, thereby resulting in lower AWSD and friction coefficient than CB contaminated liquid paraffin. Moreover, the preferentially absorbed antiwear additives (ZDDP) and the  $\text{TiF}_3$  catalyst that formed the protective films prevented carbon black from making contact with the steel surface

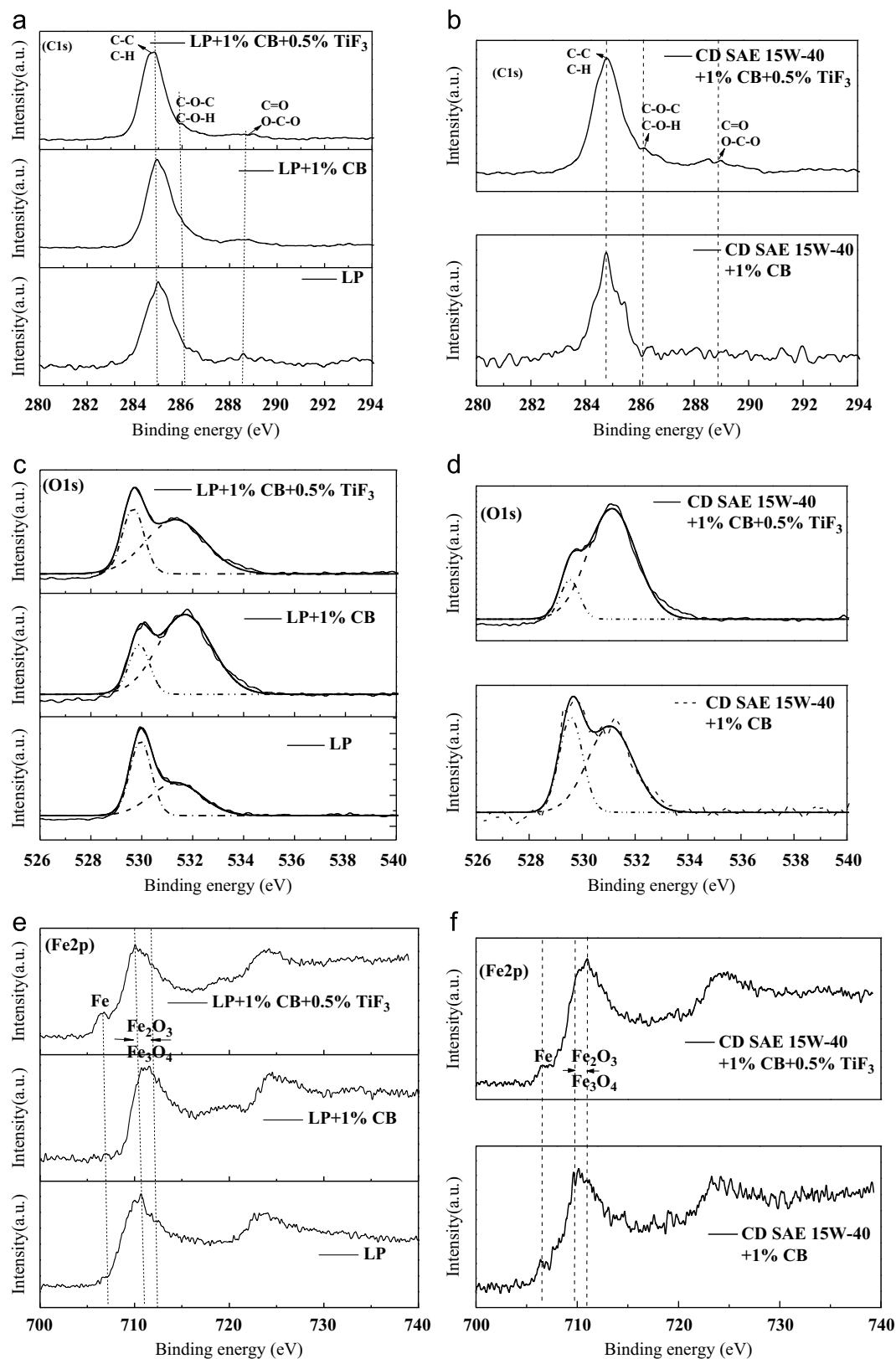


Fig. 6. Chemical valence state of chemical in wear zones in the two kinds of carbon black-contaminated engine oils.

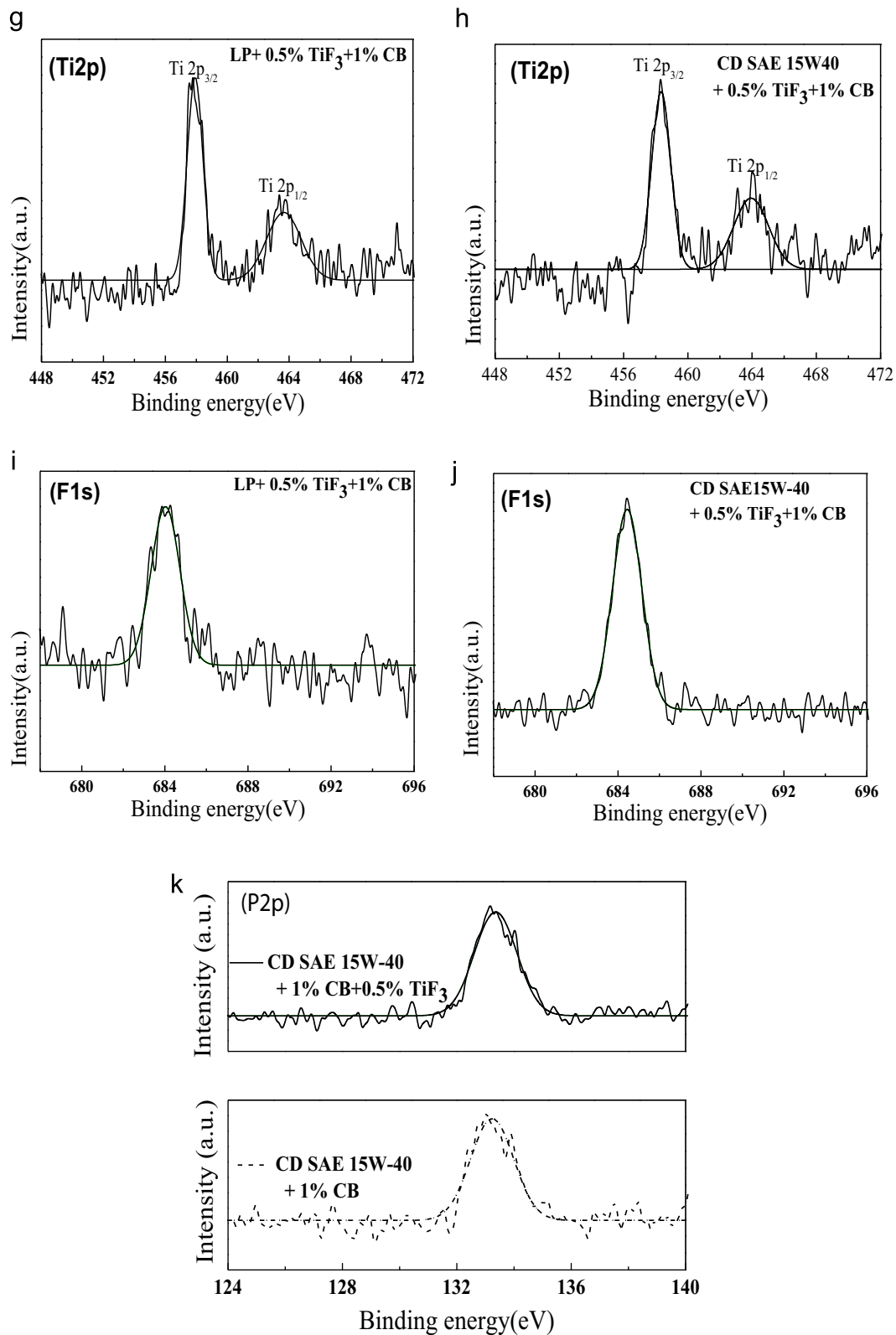


Fig. 6. (continued)

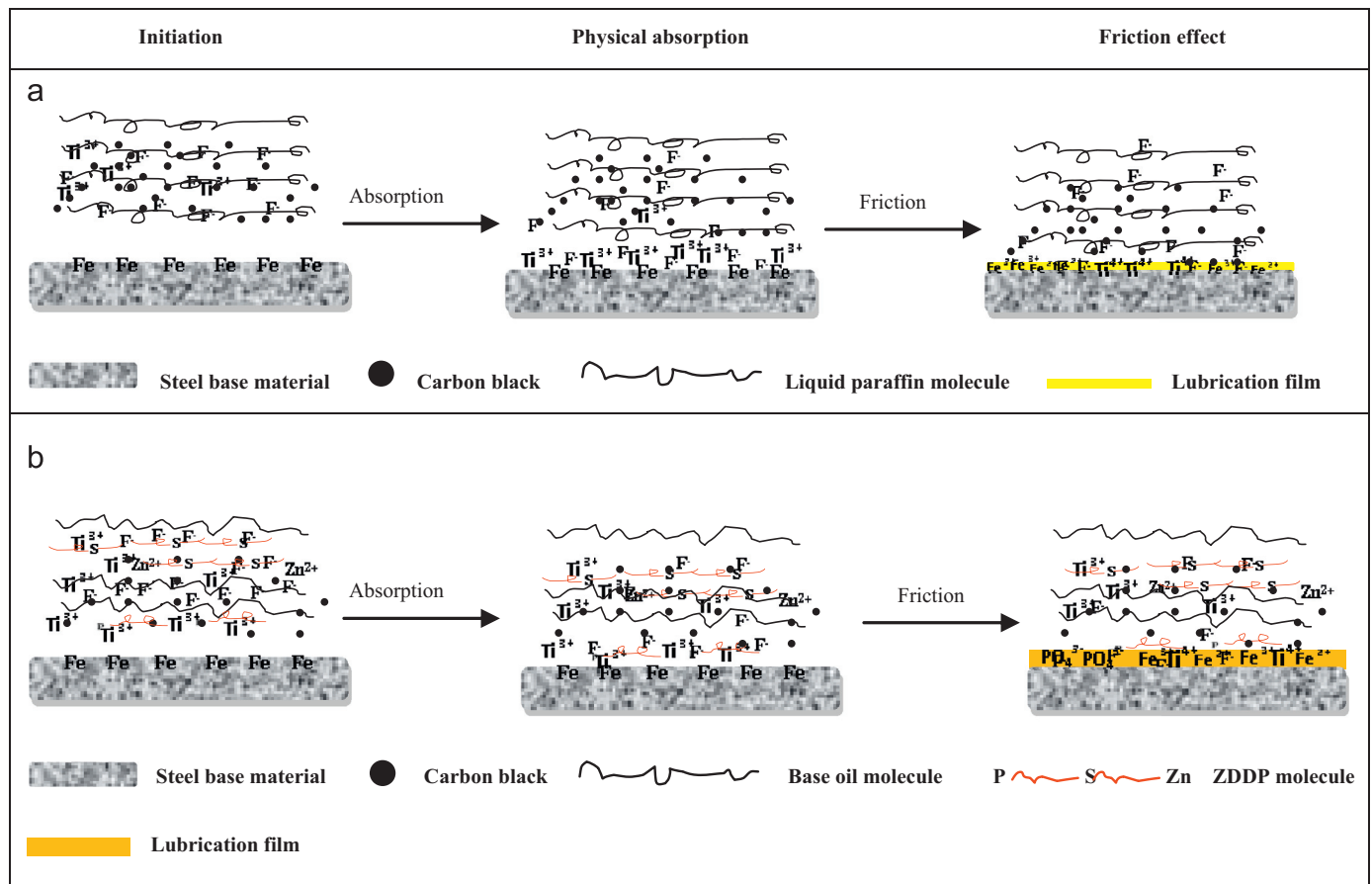
[38]. During the rubbing process, ZDDP degraded into a glassy-state polyphosphate under the friction force as well as the frictional thermal and the catalytic conditions [20,41–44]. This finding was confirmed by the X-ray photo-electron spectroscopy results showing the phosphorus element in Fig. 7. The catalyzed ZDDP degradation can also be deduced by varying the initial

decomposition temperatures of the oil samples (Table 6). The change rates of the initial decomposition temperature of the CB contaminated liquid paraffin and the fully formulated engine oil were 2.5% and 13.47%, respectively. These results sufficiently prove that the TiF<sub>3</sub> catalyst played an important role in promoting the decomposition of engine oil additives such as ZDDP [45].

**Table 5**

Carbon contents of the wear zone of selective steel ball samples after rubbing for 30 min (rotation speed, 1450 rpm; load, 196 N).

Sample	Atom content (at%)		
	C(C–C)	C(C–O)	C(C=O)
LP	41.90	0	1.04
LP+1%CB	61.78	0	1.77
LP+0.5% TiF <sub>3</sub> +1% CB	53.00	5.25	3.17
CD SAE 15W-40+1% CB	32.51	17.83	0
CD SAE 15W-40+0.5% TiF <sub>3</sub> +1% CB	44.28	5.04	1.00

**Fig. 7.** Schematic diagram of tribofilm formation for liquid paraffin and CD SAE 15W-40 oil.**Table 6**Initial decomposition temperature of engine oils with and without TiF<sub>3</sub> catalyst.

Items	Initial decomposition temperature (°C)
LP+1% soot	248.0
LP+1% soot+0.5% TiF <sub>3</sub>	241.8
CD SAE 15W-40+1% soot	309.5
CD SAE 15W-40+1% soot+0.5% TiF <sub>3</sub>	267.8

#### 4. Conclusions

- (1) The TiF<sub>3</sub> catalyst material makes an important contribution to enhancing the antiwear and antifriction properties

of engine oils and in the presence of low levels of contamination.

- (2) The average wear scar diameter and friction coefficient of two kinds of carbon black-contaminated engine oils decreased in the presence of 0.5 wt% TiF<sub>3</sub>. The variation in the average wear scar diameter of CB contaminated liquid paraffin and the fully formulated engine lubricant were 29.45% and 11.54%, respectively.
- (3) The antiwear and antifriction mechanisms of the TiF<sub>3</sub> catalyst material were attributed to titanium and fluorine elements that themselves assisted in the formation of a boundary lubrication film.
- (4) The TiF<sub>3</sub> catalyst played an important role in promoting the decomposition of antiwear additives within the engine lubricating oil. The friction functional transition of the

simulated soot particles and the thermal stability of engine oils should be further investigated in the presence of a  $\text{TiF}_3$  catalyst material.

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## References

- [1] R. Calabria, F. Chiariello, P. Massoli, Combustion fundamentals of pyrolysis oil based fuels, *Experimental Thermal and Fluid Science* 31 (2007) 413–420.
- [2] A. Williams, J.M. Jones, L. Ma, M. Pourkashanian, Pollutants from the combustion of solid biomass fuels, *Progress in Energy and Combustion Science* 38 (2012) 113–137.
- [3] E.G. Giakoumis, C.D. Rakopoulos, A.M. Dimaratos, D.C. Rakopoulos, Exhaust emissions with ethanol or *n*-butanol diesel fuel blends during transient operation: a review, *Renewable and Sustainable Energy Reviews* 17 (2013) 170–190.
- [4] A.K. Agarwal, Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines, *Progress in Energy and Combustion Science* 33 (2007) 233–271.
- [5] M.S. Michio Ikura, Ed. Hogan, Emulsification of pyrolysis derived bio-oil in diesel fuel, *Biomass and Bioenergy* 24 (2003) 221–232.
- [6] D.R. Tree, K.I. Svensson, Soot processes in compression ignition engines, *Progress in Energy and Combustion Science* 33 (2007) 272–309.
- [7] S. Aldajah, O.O. Ajayi, G.R. Fenske, I.L. Goldblatt, Effect of exhaust gas recirculation (EGR) contamination of diesel engine oil on wear, *Wear* 263 (2007) 93–98.
- [8] S.O.K. Ishiki, M. Takiguchi, M. Urabe, A Study of Abnormal Wear in Power Cylinder of Diesel Engine with EGR—Wear Mechanism of Soot Contaminated in Lubricating oil, *SAE Technical Paper* 2000-01-0925.
- [9] M. Ratoi, R.C. Castle, C.H. Bovington, H.A. Spikes, The influence of soot and dispersant on ZDDP film thickness and friction, *Lubrication Science* 25 (2004) 25–43.
- [10] L. Joly-Pottuz, J.M. Martin, B. Vacher, J. Igarashi, Wear Mechanisms of Steel under Boundary Lubrication in Presence of Carbon Black and Graphite Nanoparticles, *SAE Technical Paper* 2008-01-2461.
- [11] Y. Olomolehin, R. Kapadia, H. Spikes, Antagonistic interaction of antiwear additives and carbon black, *Tribology Letters* 37 (2009) 49–58.
- [12] D.A. Green, R. Lewis, Effect of soot on oil properties and wear of engine components, *Journal of Physics D: Applied Physics* 40 (2007) 5488–5501.
- [13] D.A. Green, R. Lewis, R. Dwyer-Joyce, Wear of Valve Train Components Due to Soot Contaminated Lubricant, *SAE Technical Paper*, no: 2006-01-1098.
- [14] R. Lewis, D.A. Green, The effects of soot-contaminated engine oil on wear and friction: a review, *Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering* 222 (2008) 1669–1689.
- [15] E.S. Yamaguchi, M. Utermann, S.H. Roby, S.H. Ryason, S.W. Yeh, Soot wear in diesel engines, *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology* 220 (2006) 463–469.
- [16] I. Berbezier, J.M. Martin, P. Kapsa, Role of carbon in lubricated mild wear, *Tribology International* 19 (3) (1986) 115–122.
- [17] S. George, S. Balla, M. Gautam, Effect of diesel soot contaminated oil on engine wear, *Wear* 262 (2007) 1113–1122.
- [18] T.C. Jao, S. Li, K. Yatsunami, S.J. Chen, A.A. Csontos, J.M. Howe, Soot characterisation and diesel engine wear, *Lubrication Science* 16 (2004) 111–126.
- [19] E. Hu, X. Hu, T. Liu, Y. Liu, R. Song, Y. Chen, Investigation of morphology, structure and composition of biomass-oil soot particles, *Applied Surface Science* 270 (2013) 596–603.
- [20] G. Nehme, Effect of extreme load on plain ZDDP oil in the presence of  $\text{FeF}_3$  catalyst using design of experiment and fundamental study under two different rotational speeds, *Tribology Transactions* 55 (2012) 829–845.
- [21] G. Nehme, The effect of  $\text{FeF}_3/\text{TiF}_3$  catalysts on the thermal and tribological performance of plain oil ZDDP under extreme pressure loading, *Wear* 278–279 (2012) 9–17.
- [22] R.L. Elsenbaumer, Pranesh B. Aswath, Gabi Nehme et al., University of Texas at Arlington and Platinum Research Cooperation, European Coating Conference: Smart Coatings II Berlin Germany: June 16, 2003. Sponsored by Vincentz Verlag KG. High Performance Lubricants and Coatings by Catalyzed PTFE Modification of the Metal Surfaces, 16 2003 pp. 1–10.
- [23] R. Mourhatch, P.B. Aswath, Tribological behavior and nature of tribofilms generated from fluorinated ZDDP in comparison to ZDDP under extreme pressure conditions—Part 1: Structure and chemistry of tribofilms, *Tribology International* 44 (2011) 187–200.
- [24] R. Mourhatch, P.B. Aswath, Tribological behavior and nature of tribofilms generated from fluorinated ZDDP in comparison to ZDDP under extreme pressure conditions—Part II: Morphology and nanoscale properties of tribofilms, *Tribology International* 44 (2011) 201–210.
- [25] Z. Huq, P.B. Aswath, R.L. Elsenbaumer, TEM studies of anti-wear films/wear particles generated under boundary condition lubrication, *Tribology International* 40 (2007) 111–116.
- [26] K. Parekh, X. Chen, P.B. Aswath, Synthesis of fluorinated ZDDP, *Tribology Letters* 41 (2009) 141–153.
- [27] H. Shaub, P.B. Aswath, Z. Huq, Engine Oil Additive, US Patents, no: 7074745, 2006.
- [28] P.B. Aswath, H. Shaub, R. Mourhatch, K. Patel, D. Owen, R. Elsenbaumer, High Performance Lubricant Additives for Crankcase Oils, Greases, Gear Oils and Transmission Oils, US Patents, no: 7754662, 2010.
- [29] F.C. Greer, Catalyzed Surface Composition Altering and Surface Coating Formulations and Methods, U.S. Patents, no: 6258758B1, 2001.
- [30] F.G. Rounds, Soots from Used Diesel Engine Oils—Their Effects on Wear as Measured in 4-ball Wear Tests, *SAE Paper* no: 810499, 1981.
- [31] E. Hu, X. Hu, X. Wang, Y. Xu, K. Dearn, H. Xu, On the fundamental lubricity of 2,5-dimethylfuran as a synthetic engine fuel, *Tribology International* 55 (2012) 119–125.
- [32] E. Hu, X. Hu, T. Liu, L. Fang, K.D. Dearn, H. Xu, The role of soot particles in the tribological behaviour of engine lubricating oils, *Wear* 304 (2013) 152–161.
- [33] D.A. Green, R. Lewis, R.S. Dwyer-Joyce, Wear effects and mechanisms of soot-contaminated automotive lubricants, *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology* 220 (3), 159–169.
- [34] D.A. Green, R. Lewis, Investigation of Soot Contaminated Lubricant Wear Mechanisms, *SAE Technical Paper*, no: 2007-01-1964.
- [35] E. Hu, Y. Xu, X. Hu, L. Pan, S. Jiang, Corrosion behaviors of metals in biodiesel from rapeseed oil and methanol, *Renewable Energy* 37 (2012) 371–378.
- [36] Y. Xu, Q. Wang, X. Hua, C. Li, X. Zhu, Characterization of the lubricity of bio-oil/diesel fuel blends by high frequency reciprocating test rig, *Energy* 35 (2010) 283–287.
- [37] (<http://srdata.nist.gov/xps/>).
- [38] Y. Wu, B. Dacre, Effects of lubricant-additives on the kinetics and mechanisms of ZDDP adsorption on steel surfaces, *Tribology International* 30 (1997) 445–453.
- [39] Q. Xue, W. Liu, Z. Zhang, Friction and wear properties of a surface-modified  $\text{TiO}_2$  nanoparticle as an additive in liquid paraffin, *Wear* 213 (1997) 29–32.
- [40] L. Chang, Z. Zhang, C. Breidt, K. Friedrich, Tribological properties of epoxy nanocomposites: I. Enhancement of the wear resistance by nano- $\text{TiO}_2$  particles, *Wear* 258 (2005) 141–148.
- [41] G. Nehme, M. Dib, Fluorinated mix in plain ZDDP oil and commercial oil using design of experiment analysis of all interactions and fundamental study of fluorinated mix in plain ZDDP oils under 2 different r/min test cycles and extreme boundary lubrication, *Journal of Engineering Tribology* 225 (2011) 193–211.
- [42] G. Nehme, Interactions of fluorinated catalyst and polytetrafluoroethylene in two different plain zinc dialkyldithiophosphate oils and one fully formulated oil using design of experiment, *Lubrication Science* 23 (2011) 181–201.
- [43] G. Nehme, Fluorinated  $\text{FeF}_3$  catalyst interactions in three different oil formulations using design of experiment optimization and chemistry characterization of tribofilms, *Lubrication Science* 23 (2011) 153–179.
- [44] K. Hosonuma, K. Yoshida, A. Matsunaga, Decomposition products of zinc dialkyldithiophosphate in an engine and their interaction with diesel soot, *Wear* 103 (1985) 297–309.
- [45] M.Z. Huq, X. Chen, P.B. Aswath, R.L. Elsenbaumer, Thermal degradation behavior of zinc dialkyldithiophosphate in presence of catalyst and detergents in neutral oil, *Tribology Letters* 19 (2005) 127–134.